

## Spotlights on Recent JACS Publications

### ■ COLOR-CHANGING COMPLEXES FOR ANION DETECTION

Porphyrins are commonly used as building blocks for self-assembled structures, owing to their planar, rigid structures and their ability to participate in  $\pi$ - $\pi$  and  $\pi$ -ion interactions. In contrast to porphyrins, so-called expanded porphyrins display distinctive optical features, have greater flexibility, and are able to interact with anions, as opposed to cations. This difference opens up new possibilities for the creation of supramolecular assemblies for chemo-sensing applications.

Researchers led by Jonathan Sessler and Eric Anslyn report the synthesis and characterization of a series of supramolecular assemblies composed of anions in complex with expanded porphyrin molecules (DOI: 10.1021/jacs.5b03131). The highly ordered structures respond to environmental stimuli, such as exposure to polar solvents or the presence of Lewis basic anions, by undergoing changes in solubility, color, and fluorescence intensity.

Many of these changes are easily detected by the unaided eye. This ability allows researchers to differentiate readily the effect of analytes without the need for advanced analytical technologies. The team demonstrates that the self-assembled expanded porphyrin constructs can differentiate at least eight different solvents and five types of anions by simple optical means. Efforts to develop the technique for the detection of solvent vapors and to quantify the solution-based response are ongoing.

Christine Herman, Ph.D.

### ■ BUILDING STIMULI-RESPONSIVE COORDINATION STRUCTURES

Supramolecular chemists are like architects whose goal is to create complex structures from simple molecular building blocks. They draw inspiration from biology, where enzymes with intricate three-dimensional structures and unique functions abound. Allosteric enzymes are stimuli-responsive biological catalysts that undergo conformational changes upon binding to so-called effector molecules, typically resulting in dynamic modulation of catalytic activity. To create synthetic constructs that mimic allosteric enzymes, chemists have looked to transition metals to serve as hubs for joining together molecular building blocks in a modular fashion, readily yielding sophisticated supramolecular structures.

In this Perspective, Chad Mirkin and his co-authors describe a method—known as the weak-link approach—that they developed to synthesize allosteric supramolecular constructs by employing metal centers as switchable structural hinges (DOI: 10.1021/jacs.5b01054). The team summarizes two decades of progress on the weak-link approach and presents their vision for the future: that one day, chemists will be able to use the technique to build dynamically controllable catalytic structures that can be operated with high effector selectivity, and which can function in complex media, such as biological environments. They outline recent breakthroughs toward this vision, while noting that several crucial developments in the field of supramolecular coordination chemistry are necessary before

that dream can become a reality.

Christine Herman, Ph.D.

### ■ RATIONALLY TWISTED CHIRAL NANOSTRUCTURES

Wei Qi and colleagues have discovered a new way to direct the hierarchical self-assembly of a modified dipeptide into a variety of tailored nanostructures (DOI: 10.1021/jacs.5b03925). Chiral nanostructures are an emerging class of materials with applications in biomedicine, catalysis, and optics. One way to make them is by exploiting the self-assembly of proteins and DNA. Ideally, scientists would like to use simple peptides as building blocks for the rational design of chiral nanostructures. But this goal presents a challenge because simple peptides often fold into achiral secondary structures that stymie the formation of more complex chiral molecules.

Now Qi and colleagues present a strategy for rationally designing a fleet of chiral nanostructures from a ferrocene-modified derivative of the diphenylalanine peptide, which is part of the  $\beta$ -amyloid polypeptide implicated in Alzheimer's disease. The researchers vary the incorporated counterions, temperature, and solvent polarity to steer the peptide's self-assembly into seven different complex nanostructures, including twisted ribbons, nanosprings, and nanoscrews. The approach could enable greater control over the design of chiral nanostructures for use as probes, templates, and optical materials.

Deirdre Lockwood, Ph.D.

### ■ CAGED CATALYSTS STAY STRONGER LONGER

For catalysis, surface area is a key parameter. On smaller particles, more total material is exposed to the surface and accessible for reactions. More material doing catalytic work means greater catalytic efficiency. But tiny particles also tend to stick to each other or to other molecules, reversing the efficiency benefit. This apparent catch-22 has plagued those working to create catalysts that remain active and stable in solution for many reaction cycles.

To address this dilemma, previous researchers have proposed dendrimer supports for catalyst particles, as well as solid-state materials such as zeolites and metal-organic frameworks (MOFs) for added stability. Qiang Xu and colleagues instead use organic cages to surround and protect rhodium catalyst nanoparticles, including spaces between the "bars" large enough for reactants to interact (DOI: 10.1021/jacs.5b04029). The technique allows the particles to be both accessible and protected.

In experiments, the ultra-small rhodium particles remain active over many cycles, show high catalytic activity, and remain stable and dispersed in solution. The researchers also recover the catalysts intact with simple drying and washing. This strategy is not limited to rhodium catalysts and could easily be expanded to other kinds of nanoparticles in need of strategies that marry the benefits of high reactivity and solution stability.

Jenny Morber, Ph.D.

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